(54) PALLADIUM COMPOSITIONS SUITABLE AS OXIDATION CATALYSTS

(71)   We, LAROX RESEARCH CORPORATION a Corporation organized and existing under the laws of the State of Kentucky of 1419 Woodhurst Drive, Bowling Green, Warren County, Kentucky, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention has to do with compositions containing a palladium (II) salt, a copper (II) halide and a non-halide copper (II) salt. The compositions are effective oxidation catalysts, particularly for the oxidation of CO to CO_2, and SO_2 to SO_3.

In recent years, considerable attention has been given to methods for removing CO and SO_2 from our environment. CO is a pollutant, particularly as an exhaust product from motor vehicles. In the United States, the transportation industry is responsible for 42% of the total air contaminants emitted to the atmosphere; and carbon monoxide, a colorless, odorless and lethal gas, being one of the major components of automobile exhausts, is the largest single air pollutant. Of the 90.5 million tons of carbon monoxide emitted in 1968 to the atmosphere, 63.8 million tons or 17% came from transportation activities. SO_2 is also a pollutant, but generally as a product from the burning of relatively high sulfur heating oils and coals.

The oxides of sulfur in the U.S. in 1968 accounted for an estimated 33 million tons, or 15—16% of the total emitted air contamination. Of this, fuel combustion by stationary sources accounted for 24.4 million tons or 74% of the total oxides of sulfur. The most important air pollutants among the oxides of sulfur are sulfur dioxide, SO_2, and sulfur trioxide, SO_3. The estimated ratio of SO_2 to SO_3 in the atmosphere of Chicago is 100:1. The conversion of SO_2 to SO_3 in air is very slow. The major source of SO_2 is from the combustion of sulfur-containing fuels.

The present invention is directed to the provision of new and superior oxidation catalysts which are particularly effective for the conversion of CO to CO_2 and SO_2 to SO_3.

In accordance with the present invention, there is provided an aqueous homogeneous solution which comprises:

(a) a water-soluble palladium (II) salt having a concentration of palladium ion of 0.00005 to 0.025 mole per liter,

(b) a copper (II) chloride or bromide, and

(c) a copper (II) salt of an oxyanion derived from a strong acid (as hereinafter defined), wherein the total concentration of (b) and (c) is from 0.003 to 3 moles per liter, and wherein the copper halide comprises from 15 to 60 mole percent of the total of (b) and (c).

There is also provided a catalyst composition obtained by impregnating a support with a solution as defined above, and drying the impregnated support, which comprises from 0.0003 to 0.03 moles per kilogram of the palladium (II) salt.

There are also provided processes for oxidizing CO and SO_2 to CO_2 and SO_3, respectively, by contacting a gaseous charge containing CO and/or SO_2 with a catalyst of the character specified above, at a temperature of from 0 to 100°C for the aqueous catalysts and from 0 to 300°C for the catalysts with a support.

As indicated above, the compositions of this invention contain a water-soluble palladium (II) salt, such salts either dissolve in water or are able to be dissolved as with the aid of a supporting electrolyte. Stated in another manner, the palladium salts are those soluble in halide-containing aqueous solutions. Typical of such salts are the: chloride, bromide, nitrate, sulfate and Li_2PdCl_4. Particularly preferred is palladium (II) chloride.

The concentration of the palladium (II) salt in the homogeneous solutions can range from 0.00005 to 0.025 mole per liter. Pre-

ferred concentrations range from 0.001—0.02 mole per liter.

A mixture of copper (II) salts (b) and (c), is employed. One salt (b) is the chloride or bromide. The chloride is preferred. The other salt (c) is a non-halide, and is a salt of an oxyanion derived from a strong acid.

The expression "strong acid" as used herein means an acid of which a 0.1 molar aqueous solution is predominantly dissociated.

Typical of (c) are: nitrate, sulfate, alkylsulfonate (e.g. methanesulfonate), trifluoromethanesulfonate, aryl sulfonate (e.g. p-toluenesulfonate), tetrafluoroborate, perchlorate, trifluoroacetate, trichloroacetate and methanephosphonate.

The total concentration of the copper (II) salts (b) and (c) is from 0.003 to 3, and preferably 0.1 to 2.0 moles per liter. Solutions with very low copper (II) concentrations, below 0.003M, are limited in the rate at which reduced palladium (0) can be reoxidized, and in unfavourable operating conditions may precipitate reduced palladium metal, removing it from the homogeneous system with consequent loss of catalytic activity. At copper (II) salt concentrations above approximately 3 moles per liter two disadvantageous factors emerge: increased solution viscosity which impairs the ease and efficiency of gas-liquid mixing, and the possibility of exceeding salt solubilities and precipitating catalyst or co-catalyst under actual operating conditions in which water evaporation may involve fluctuations in water content.

A critical relationship of the aqueous homogeneous catalysts is the balance of copper (II) halide (b) and the other copper (II) salt (c). It has been found, according to the invention, that superior results are realized by employing 15—60, mole percent of salt (b) of the total of (b) and (c), with (c) the remainder. The chloride ion concentration is substantially 0.2—0.7, times the weight of copper (II); or, when bromide ion is present instead of chloride ion, the bromide ion concentration is substantially 0.4—1.5, times the weight of copper (II) present.

As mentioned above, the palladium (II) salt can be in the form of Li_2PdCl_4. Thus, LiCl in association with $PdCl_2$ serves to facilitate dissolution of $PdCl_2$ in water. In this regard, it has been found that when $PdCl_2$ and LiCl are added to a solution containing copper (II) salts (b) and (c), the resulting solution is effective as an oxidation catalyst; however, when the resulting solution is allowed to age at ambient temperature (20—25°C.) for approximately three hours or more, it is substantially more effective as an oxidation catalyst.

In addition to the palladium (II) salt (a) and the copper (II) salts (b) and (c), the homogeneous solutions can also contain a compatible chloride or bromide salt to aid in the dissolving of the palladium (II) salt. Chloride and bromide salts of Group IA and Group IIA metals, for example, have no adverse effect upon the catalytic activity of the solutions. The solutions can also contain any other dissolved salts which are compatible with the palladium (II) and copper (II) salts, that is, which do not form specific complexes or precipitates of copper (II) or palladium (II).

The solutions are prepared by adding the salts (a), (b) and (c), with or without a chloride or bromide salt of a Group IA and/or Group IIA metal, to water in the concentration specified above. Other than the aging effect already mentioned with respect to a solution containing LiCl, the particular order of addition of salts (a), (b) and (c) to water has no substantial influence upon the catalytic effectiveness of the resulting solution.

When the homogeneous catalysts are employed for the oxidation of CO to CO_2 and SO_2 to SO_3, the temperature used can be approximately 0—100°C., and preferably at 10—50°C., at atmospheric pressure. Variation in pressure can range from subatmospheric (the limit being the vapor pressure exerted by the catalyst solution) through to superatmospheric, with the preferred pressure being at or near atmospheric pressure.

Flow rates depend upon the geometry of the apparatus employed. Contact time will range generally from 0.1—5 seconds, with a preferred range of 0.3—3 seconds.

The CO partial pressure can be any fraction of the total gas pressure. CO removal at partial pressures as low as 4×10^{-5} atmospheres, which is the limit of the detection system employed, has been accomplished. For SO_2, any partial pressure which does not liquify it is acceptable. With the preferred total pressure close to atmospheric, the preferred partial pressures of these reactant gases are 0—0.5 atmospheres.

If there should be less than a stoichiometric excess of oxygen in the feed gas (with respect to CO and/or SO_2), then the catalyst solution should be contacted periodically with an oxygen-containing gas, such as air, in order to reoxidize copper (I) and retain catalyst activity. This can be done by continuous recycling or batch treatment.

The heterogeneous catalysts of this invention comprise a support material impregnated with specified amount of the palladium (II) salt (a) and of the copper (II) salts (b) and (c). Here again, the water-soluble palladium (II) salts (a) and copper (II) salts (b) and (c), above, are employed. Typical supports include alumina, silica, silica/alumina, zirconia, thoria, alumino silicates, zeolites, magnesia, silicon carbide and the like. Such supports are well known in the art and are available commercially. Particularly useful are

those supports which can be used at temperatures generally existing in vehicle exhaust systems and industrial stacks.

The supported catalysts are prepared by contacting an aqueous homogeneous solution with a suitable support, and slurrying the solution with the support at 0°C.—300°C., preferably 60—150°C., for 5—60 minutes. The support which has become impregnated with the solution is separated from the remaining solution, as by suction filtration, and is dried. Drying can be accomplished with an aspirator air stream for several minutes, then by keeping the impregnated support under vacuum (e.g. 20 mms.) at 20—25°C. for 16 hours, followed by approximately 24 hours at 20 mins. vacuum at 60°C. There is no need to calcine the catalyst.

The resulting supported catalysts will contain: 0.0003—0.03, moles of palladium (II) salt per kilogram of inert support, and the total copper (II) salts are generally from 0.001—1.5, preferably 0.03—0.8, moles per Kg, with the same ratio of (b)/(c) as specified above. The chloride and bromide concentrations are the same as those given above for homogeneous catalysts.

Here also, a salt of a Group IA or Group IIA metal which does not cause precipitation of a copper or palladium salt, can be employed.

The heterogeneous catalysts can be employed in oxidation reactions, and particularly for converting CO to CO_2 and SO_2 to SO_3, at temperatures of the approximate range of 0—300°C. and preferably from ambient temperature to 150°C.

Total pressure can be atmospheric, sub- and superatmospheric, with those approximating atmospheric being preferred.

With regard to gas flow rates, a minimum of approximately 0.1 second contact time is employed. An upper limit is governed by considerations of practical economics (and upon how rich the gas stream is in oxidizable contaminant gases). Preferred contact times are 0.3—3.0 seconds.

With employment of the heterogeneous catalysts, it is recommended that molecular oxygen also be included in the reaction system. In order to have catalyst lifetimes of practical duration, molecular oxygen is present in at least stoichiometric quantities in the gas stream being treated.

The homogeneous solutions and oxidation reactions therewith, are illustrated by the following examples.

EXAMPLE 1.

To a 500-m. gas-scrubbing bottle fitted with a standard coarse glass diffusing frit was added 100 mL. of an aqueous solution. A mixture of helium 98% and carbon monoxide 2.00% was then passed through the diffusing frit at atmospheric pressure and at 23°C. The gas flow rate was 640 ± 40 ml./min. and the mean gas-liquid contact time (based upon solution and overhead foam volume) was 1.9 ± 0.1 sec. Samples of exit gas were collected at 9.0 minutes and again at 10.0 minutes after the gas flow was started; these were analyzed by quantitative gas chromatography for carbon monoxide and for carbon dioxide. The results, expressed for various aqueous solutions as percent conversion of CO to CO_2, are shown in TABLE I below and in the drawing.

The aqueous solutions were prepared by dissolving $PdCl_2$, $LiCl$, $CuCl_2$ and $Cu(NO_3)_2$ in water at 20—25°C.

TABLE I

Total Cu salt	$PdCl_2$	LiCl	$CuCl_2$ % of total Cu salt	$Cu(NO_3)_2$ % of total Cu salt	% Conversion of CO to CO_2	No.
1.00 M	.0010 M	.0020 M	100	nil	nil[a]	1
1.00	.0010	.0020	80	20	nil[a]	2
1.00	.0010	.0020	60	40	0.4	3
1.00	.0010	.0020	40	60	4.2	4
1.00	.0010	.0020	20	80	58.	5
1.00	.0010	.0020	nil	100	nil[a]	6
0.97	.0040	.0080	100	nil	26.	7
0.97	.0040	.0080	80	20	41.	8
0.97	.0040	.0080	60	40	72.	9
0.97	.0040	.0080	40	60	85.[b]	10
0.97	.0040	.0080	20	80	78.[c]	11
0.97	.0040	.0080	nil	100	0.8	12

[a]No detectable CO_2; threshold of detection is 0.2% conversion level.

[b]A white precipitate of cuprous hydroxide was formed after 10 minutes' operation.

[c]A white precipitate of cuprous hydroxide and a dark precipitate of Pd and/or PdO was formed after 10 minutes' operation.

EXAMPLE 2.

The apparatus and procedure of EXAMPLE 1 was employed. Gas flow rate ras regulated at 630 ± 10 ml. of CO per minute. All runs were conducted at 23°C. LiCl concentration in each run was approximately twice the concentration of the palladium or rhodium chloride concentration.

$PdCl_2$ was compared with $RhCl_3$. Various combinations of cupric salts were used. Comparison is also given of ferric salts and of organic redox compounds, in place of the cupric salts.

Results are provided in TABLE II.

TABLE II

Pd or Rh	Cupric Salts, etc.	gas-liquid contact time	% Conversion of CO to CO₂	#
nil	$CuCl_2$ 0.50M, $Cu(NO_3)_2$ 0.50M	1.5 sec.	nil[a]	1
$PdCl_2$ .005M	$CuCl_2$ 0.50M, $CuSO_4$ 0.50M	1.6	31%	2
$PdCl_2$ .005M	$CuBr_2$ 0.50M, $Cu(NO_3)_2$ 0.50M	1.9	32%	3
$RhCl_3$ .005M	$CuCl_2$ 0.50M, $Cu(NO_3)_2$ 0.50M	1.3	nil	4
$PdCl_2$ .005M	$FeCl_3$ 0.50M, $Fe(NO_3)_3$ 0.50M	2.5	≃0.4%	5
$PdCl_2$ .005M	p-Benzoquinone 2.0M in 1,2-propanediol	...	≃0.4%	6
$PdCl_2$ .0025M	p-Benzoquinone 1.0M in a 1 : 1 mixture (vol/vol) of ethanol and 1,2-propanediol	2.	15%	7
$PdCl_2$ .005M	$CuCl_2$ 0.50M, $Cu(NO_3)_2$ 0.50M [fresh mixed with Pd salt]	1.3	17%	8
$PdCl_2$ .005M	$CuCl_2$ 0.50M, $Cu(NO_3)_2$ 0.50M [after three hours' standing]	1.3	82%	9

[a]No detectable CO_2; threshold of detection is ≃0.2%.

EXAMPLE 3.

A series of runs was carried out in which 1.5 liters of an aqueous solution was mixed vigorously with sulfur dioxide gas at 1.0 atm. pressure, for 20 minutes at 24°C. Mixing was accomplished by churning with a gas-liquid mixing device in a 3.0-liter glass flask, adding make-up sulfur dioxide to the gas phase continuously so as to maintain pressure. The solution was then degassed by agitation under reduced pressure for five minutes, purged with air, refluxed for 30 minutes, cooled, and aliquots withdrawn and titrated with standard base to determine acid normality.

Under this regimen the dissolved SO_2 is very substantially removed, so that in the case of no oxidation (see Run No. 1), the acid concentration in the degassed solution is very low. To the extent that oxidation of SO_2 has occurred, however, sulfuric acid will have been formed, and this acid cannot be removed from aqueous solutions by any degassing techniques. The extent of formation of sulfuric acid, as measured by the development of permanent acidity, measures the extent of oxidation of sulfur dioxide.

Run No. 1. This run was carried out with 1.5 liters of water. The water was completely saturated with sulfur dioxide within 15 minutes. After degassing, titration of aliquots with a standard base showed the residual acidity (due to sulfurous acid) to be 0.015 N (± 0.001).

Run No. 2. This run was carried out as Run No. 1, except that the water was replaced with 1.5 liters of an aqueous solution containing 0.50M cupric chloride and 0.50M cupric sulfate. After treatment as in Run No. 1, the gross titratable acidity was found to be 2.006 N (± 0.006). After correcting for the effective acidity of the cupric salts, the net gain in acidity upon 20 minutes' contact with SO_2 was 0.39N.

Run No. 3. This was carried out in the same manner as Runs Nos. 1 and 2, except that 1.5 liters of aqueous solution containing 3.55×10^{-3} M palladous chloride, 0.50M cupric chloride, and 0.50M cupric sulfate. The gross titratable acidity was found to be 2.641 (±0.013), which after correcting for the effective acidity of the salts showed a net gain of 0.96 N. This amount of formed acid is approximately 2-1/2 fold greater than that in Run No. 2 and approximately sixty-fold greater than that in Run No. 1.

EXAMPLE 4.

A stream of helium containing 2 × 10 ppm CO was passed through an aqueous solution containing 0.020 M $PdCl_2$, 1.00 M $CuCl_2$, and 1.00 M $Cu(NO_3)_2$. In each of three standard gas-washing bottles (250 ml capacity, fitted with coarse fritted glass diffusers) was placed 150 ml of catalyst solution, and the three bottles were connected in series down stream of a flowmeter connected to a cylinder

containing the helium-carbon monoxide mixture. The cylinder valve was set to permit a flow of 235 ml/min through the system. After 25 min. of operation at 22°C., a portion of untreated feed gas was then collected for comparison.

The gas samples were analyzed by gas chromatography, with a standard thermal conductivity instrument (Aerograph Model 202—1C) fitted with a 6 ft. × 1/4 in. column of Porapak Q for carbon dioxide assay and a 6 ft. × 1/4 in. column of molecular sieve 5A for carbon monoxide assay, both determinations run at a column temperature of 30°C. "Aerograph" and "Porapak" are registered Trade Marks. Assays were made in quadruplicate, with retention of the best three of each set of four determinations.

Data is given below in Table III, showing that the CO content of the gas mixture is reduced from 2.0 to 0.06% at the same time time that a major CO_2 peak appears, as a result of passage through the catalyst system. Cross analysis of the untreated gas shows the presence of a small amount of CO_2, about 0.05%, as an initial impurity.

This study, with an effective gas-liquid contact time of about 1.5 sec., shows that a gas stream containing 2×10^4 ppm carbon monoxide can be treated to effect conversion of 97% of the CO to CO_2.

TABLE III

Gas Chromatographic Analyses of Gas Mixture

	CO, %	CO_2, %
	1.96	0.06_2
Feed Gas	2.02 (av. 2.00%)	0.03_1 (av. 0.05%)
	2.02	0.04_6
Effluent Gas	0.05_8	2.03
	0.07_1 (av. 0.06%)	2.00 (av. 2.00%)
	0.05_0	1.97
SD of analysis:	overall ± 0.021% as CO (8 DF)	
	low range ± 0.010% as CO (4 DF)	

Heterogeneous catalysts and oxidation reactions therewith, are illustrated by the following examples.

EXAMPLE 5.

Four solid catalyst systems were prepared by contacting portions of an aqueous catalyst solution with each of the following: (a) Molecular Sieve 5A, a crystalline alumina-silicate marketed by Union Carbide; (b) silica gel; (c) activated alumina, and (d) activated charcoal Norit "A" marketed by Matheson Coleman & Bell ("Norit" is a Registered Trade Mark). The catalyst solution comprised: $PdCl_2$, 0.01 M; LiCl, 0.02 M; $CuCl_2$, 0.788 M; $Cu(NO_3)_2$, 0.98M, and the balance water.

To 50-ml. portions of the above catalyst preparation solution were added 10.0-g. portions of each of several solid catalyst supports, described in Table IV below. The mixtures were slurried for 15 minutes at room temperature, then the solids were collected by suction filtration and dried for five minutes by an aspirator air stream. Then, the resulting moist cakes were broken up and the solids dried overnight at 20 mm. pressure. The solids were then further dried at 60°C. and 20 mm. pressure for an additional 24 hours. Each supported catalyst powder was then weighed to determine the amount of catalyst picked up, then packed into a copper column 36 inches long and 0.190 inch internal diameter, closed with loose glass-wool plugs to prevent catalyst loss.

The pickup of weight for each of four catalyst supports, and the indicated concentrations of components per kilogram of catalyst support, is:

Support	Wt. gain after drying, per 10 g. of support	Calculated concentrations, moles/Kg support			
		PdCl₂	CuCl₂	Cu(NO₃)₂	LiCl
Alumina	1.0	.0034	.270	.335	.0068
Norit A	1.0	.0034	.270	.335	.0068
Molecular Sieve	2.8	.0096	.755	.938	.0190
Silica	2.8	.0096	.755	.938	.0190

The average weight increase of each support is 19%. It appears that the concentration of palladium (II) in each of the four catalysts is 0.003—0.01 moles/Kg support.

In the experiments, a stream of helium containing 2.00% carbon monoxide (CO) and a stream of compressed air were combined in an atmospheric pressure manifold, and the resulting mixed stream was passed through a standard 500 ml. gas sparger containing 150 ml. of water, thus humidifying the gas mixture. The gas mixture was then passed through a section of copper tubing (36 inches by 0.250 inch outside diameter, 0.190 inch inside diameter, and with approximately 24 inches of the length packed with the solid catalyst-and-support combination being tested), and then to an exit vent from which samples were periodically withdrawn. For a control run with no supported catalyst, the exit sample was withdrawn immediately downstream of the humidifying gas sparger. Crude flow controls of the air and the helium-CO streams were accomplished by floating ball flowmeters; how-

ever, the actual amount of air in the gas mixture was determined more accurately in the course of gas chromatographic analysis of the exit gas samples.

Gas chromatographic analysis was obtained on samples collected in standard 125 ml. gas collection flasks which were evacuated immediately prior to sampling. Analysis was carried out with 2.00 ml. gas samples using a parallel-column assembly (Porapak Q packing in one leg, 10 ft. × 1/4 inch, and Molecular Sieve in the other leg, 4 ft. × 1/4 inch) at 130°C. injector 165°C., detector (thermal conductivity, at 150 milliamperes) 240°C., and a helium flow rate of 50 ml./min.

The results of these runs are shown in TABLE IV below. Except for the control run, which showed no detectable conversion, eight runs with four solid supports show CO conversions of from 2% to 100%.

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TABLE IV

Catalyst Support (a)	Time on stream	% Air in Feed Gas (a)	Gas-Catalyst Contact Time (b)	% Conversion of CO to CO_2 (c)
Molecular Sieve 5A, 80/100 mesh	20 min.	15.	1.7	60% (61,59)
,, ,, ,,	47 min.	3.	2.0	54% (52,53)
Silica Gel, Grade 12, 28/200 mesh	15 min.	8.	1.7	2% (2,2,2)
,, ,, ,,	37 min.	7.	1.8	44% (43,44)
,, ,, ,,	51 min.	4.	2.0	51% (50,51)
Alumina, Chromatographic Grade 80/325 mesh	20 min.	29	100.	95% (94,95)
,, ,, ,,	40 min.	23	115.	100% (d) (100,100)
Charcoal, Norit "A", fine powder	47 min.	64%	160.	100 (d) (100,100)
Control (no catalyst)	—	13%	—	nil (e)

(a) Determined by quantitative gas chromatography of the exit gas.

(b) Based upon the estimate that 70% of tubing internal volume is filled by catalyst and solid support: contact time = 0.30 × (nominal tube volume)/(flowmeter flow rate).

(c) Determined by quantitative gas chromatography; figures in parentheses are replicate individual determinations.

(d) No detectable residual CO: threshold of detection is about 0.2% of the feed concentration.

(e) No detectable CO_2; threshold of detection is about 0.3% of the feed concentration of CO for these experiments.

WHAT WE CLAIM IS:—

1. An aqueous homogeneous solution which comprises:

(a) a water-soluble palladium (II) salt having a concentration of palladium ion of 0.00005 to 0.025 mole per liter,

(b) a copper (II) chloride or bromide, and

(c) a copper (II) salt of an oxyanion derived from a strong acid (as hereinbefore defined), wherein the total concentration of (b) and (c) is from 0.003 to 3 moles per liter, and wherein the copper halide comprises from 15 to 60 mole percent of the total of (b) and (c).

2. A solution in accordance with Claim 1, wherein the palladium salt (a) is palladium (II) chloride.

3. A solution in accordance with Claim 1 or Claim 2, wherein the concentration of (a) is from 0.001 to 0.02 mole per liter.

4. A solution in accordance with any Claims 1 to 3, wherein (b) is copper (II) chloride.

5. A solution in accordance with any of Claims 1 to 4, wherein the copper (II) salt (c) is a nitrate, sulfate, alkylsulfonate, arylsulfonate, tetrafluoroborate, perchlorate, trifluoroacetate, trichloroacetate or methanephosphonate.

6. A solution in accordance with any Claims 1 to 5, wherein the copper (II) salt (c) is copper (II) nitrate.

7. A solution in accordance with any of Claims 1 to 6, wherein said aqueous homogeneous solution also contains a chloride or bromide

of a Group IA or Group IIA metal.

8. A solution in accordance with any of Claims 1 to 7, wherein the palladium (II) salt is Li_2PdCl_4.

9. A solution in accordance with Claim 8, wherein said solution has been aged.

10. The process for oxidizing an oxide (A) selected from the group consisting of CO and SO_2 to the corresponding oxide (B) CO_2 and SO_3, respectively, which comprises contacting (A) at a temperature of 0 to 100°C with a solution defined by any of Claims 1 to 9.

11. The process in accordance with Claim 10 wherein (A) is CO and (B) is CO_2.

12. The process in accordance with Claim 10, wherein (A) is SO_2 and (B) is SO_3.

13. A catalyst composition obtained by impregnating a support with a solution according to any of Claims 1 to 9 and drying the impregnated support, which comprises from 0.0003 to 0.03 moles per kilogram of carrier, of palladium (II) salt.

14. A composition in accordance with Claim 13, wherein the copper (II) salt of an oxyanion derived from a strong acid is a nitrate, sulfate, alkylsulfonate, arylsulfonate, tetrafluoroborate, perchlorate, trifluoroacetate, trichloroacetate or methanephosphonate.

15. The process for oxidizing an oxide (A) selected from the group consisting of CO and SO_2 to the corresponding oxide (B) CO_2 and SO_3, respectively, which comprises contacting (A) at a temperature of 0 to 300°C with a composition defined by Claim 13 or 14.

16. The process in accordance with Claim 15, wherein (A) is CO and (B) is CO_2.

17. An aqueous homogeneous solution as claimed in Claim 1 substantially as described with reference to any of Examples 1 to 4.

18. A composition as claimed in Claim 13 substantially as described with reference to Example 5.

19. A process as claimed in Claim 10 substantially as described with reference to any of Examples 1 to 4.

20. A process as claimed in Claim 15 substantially as described with reference to Example 5.

MICHAEL BURNSIDE & PARTNERS,
Chartered Patent Agents,
Hancock House,
87, Vincent Square,
London, SW1P 2PH.
Agents for the Applicants.

Effect of Copper (II) Chloride : Copper (II) Nitrate Ratio Upon
Efficiency of Catalyst Solutions

(Total Copper Salt Concentration = 1.00 Moles per Liter)